LLNL Environmental Restoration Division Standard Operating Procedure	TITLE: QA/QC Objectives for Nonradiological Data Generated by Analytical Laboratories
APPROVAL Date _____ _____ Environmental Chemistry and Biology Group Leader	PREPARERS: V. Dibley and G. Kumamoto REVIEWERS: T. Carlsen, E. Christofferson*, B. Failor*, C. Garcia*, B. Hoppes*, S. Mathews*, P. Ottesen, M. Ridley, and B. Ward*
APPROVAL Date _____ _____ Division Leader CONCURRENCE Date _____ _____ QA Implementation Coordinator	PROCEDURE NUMBER: ERD SOP-4.6 REVISION: 2 EFFECTIVE DATE: December 1, 1995 Page 1 of 31

***Operations and Regulatory Affairs Division**

1.0 PURPOSE

This procedure specifies the criteria that analytical data must meet to ensure consistent results of a known quality and the information that must be provided by the analytical laboratory so that the data user may evaluate and make judgments based on the analytical results.

2.0 APPLICABILITY

This procedure applies to the chemical data generated by contract analytical laboratories (CALs) and on-site laboratories from the analysis of ground and surface water and soil, rock, and sediment samples that are handled by the Environmental Restoration Division (ERD) for the Environmental Protection Department.

3.0 REFERENCES

3.1 U.S. Environmental Protection Agency (EPA) (1991), *Draft National Functional Guidelines for Organic Data Review,* U.S. Environmental Protection Agency, Washington, D.C. 20460, June 1991.

3.2 EPA (1988), *Functional Guidelines for Evaluating Inorganic Analyses,* Hazardous Site Evaluation Division, U.S. Environmental Protection Agency, Washington, D.C. 20460, July 1, 1988.

3.3 EPA (1987), *Data Quality Objectives For Remedial Response Activities*, Office of Emergency Response and Office of Waste Programs Enforcement, Washington, D.C., 20460.

3.4 *Test Methods for Evaluating Solid Waste,* SW-846, November 1986, Third Edition, Chapter One—Quality Control.

4.0 DEFINITIONS

4.1 ACCURACY

The ability of a procedure to determine the "true" concentration of an analyte.

4.2 Analytical Laboratory Performance Evaluation/Check Samples

Performance evaluation samples are used to measure the performance of the laboratory on unknown samples. The results are compared to predetermined acceptance limits.

4.3 Batch

A group of 20 samples or less, of similar matrix type, prepared together or analyzed together if no sample preparation is required, under the same conditions and with the same reagents.

4.4 Blind Samples

A single blind sample is a performance check sample submitted to the laboratory as an unknown to remove the possibility of analytical bias. A double blind sample is a performance check sample, which is submitted as an unknown and is submitted by an outside source independent from the data users.

4.5 Calibration Blanks

Calibration blanks are prepared and analyzed with standards to create a calibration curve. A calibration blank should differ from other standards only by the absence of an analyte and provide the "zero-point" for the curve.

4.6 Collocated Samples

Collocated samples are independent samples collected in such a manner that they are equally representative of the parameter(s) of interest at a given point in space and time.

4.7 Duplicates

Duplicates are additional aliquots of a sample that are subjected to the same preparation and analytical scheme as the sample. The duplicate measures the precision of a given analysis and is expressed as the relative percent difference (Section 4.14 of this SOP).

4.8 Interlaboratory Collocated Samples

Interlaboratory collocated samples are collocated samples which are collected and sent to different laboratories for analysis. Interlaboratory collocated samples provide interlaboratory precision information for the entire measurement system including sample acquisition, homogeneity, handling, shipping, storage, preparation, and analysis.

4.9 Internal Standards

Internal standards are measured amounts of a certain compound added after sample preparation or extraction. They may be used in an internal standard calibration method to correct sample results suffering from instrumentation problems such as capillary column injection losses, purging losses, or the effects of viscosity. Evaluation of internal standards performance ensures the stability of sensitivity and response during each analysis.

4.10 Intralaboratory Collocated Samples

Intralaboratory collocated samples are collocated samples which are collected and sent to the same laboratory for analysis; usually one is sent as a blind sample. Intralaboratory collocated samples provide intralaboratory precision information for the entire measurement system including sample acquisition, homogeneity, handling, shipping, storage, preparation, and analysis.

4.11 Laboratory Control Standards (LCSs)

LCSs are aliquots of organic-free or deionized water to which known amounts of an analyte have been added. They are subjected to the same preparation/extraction procedure and analysis as samples. Stock solutions used for LCSs are purchased or prepared independently of calibration standards. LCS recovery indicates the accuracy of the analytical methods, equipment, and laboratory performance. For LCSs, the percent recovery is:

$$\frac{LC}{LT} \times 100$$

where:

LC = Laboratory LCS result.

LT = Expected result or true value of the LCS.

4.12 Matrix Spikes (MS)

MS are aliquots of samples to which known amounts of an analyte have been added. Stock solutions used for spiking should be purchased or prepared independently of calibration standards. Spikes are prepared and analyzed in each batch of samples and are subjected to the same preparation/extraction procedure and analysis as the samples in question. Spike recovery measures the effects of interferences from the sample matrix and reflects the accuracy of the determination. Spike recoveries are calculated as follows:

$$P = \frac{100(A - B)}{T},$$

where:

P = Percent spike recovery,
A = Concentration determined on spiked sample,
B = Concentration determined on original unspiked sample, and
T = True value of spike added.

4.13 Matrix Spike Duplicate (MSD)

An MSD measures the accuracy of the determination and the matrix effects as described in Sections 4.12 of this SOP, as well as repeatability or Relative Percent Difference of the measurements described in Section 4.19. The MS and MSD are aliquots of the same sample spiked with identical concentrations of target analytes. The MS and MSD are analyzed sequentially.

4.14 Method Blanks

Method blanks consist of organic-free or deionized water (or clean sand for soil testing) carried through the analytical scheme like a sample. They serve to measure contamination associated with laboratory storage, preparation, or instrumentation.

4.15 Outlier

An outlier is a result that falls outside of the established control limits.

4.16 Percent Relative Standard Deviation (%RSD)

A measure of precision.

$$\%RSD = \left(\frac{100}{\sqrt{2}}\right) * \left[\frac{2|R1 - R2|}{(R1 + R2)}\right],$$

where:

R1 and R2 = The reported concentrations for each duplicate sample.

4.17 Precision

The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. The most commonly used estimates of precision are the percent relative standard deviation (RSD) 4.16 of this SOP, and relative percent difference (RPD) 4.19 of this SOP.

4.18 Quality Control Samples

Samples that are introduced during the different phases of the data collection process to monitor the performance of the system.

4.19 Relative Percent Difference (%RPD)

$$\frac{(R1 - R2)}{\left[\frac{R1 + R2}{2}\right]} \times 100$$

where R1 and R2 are the result of analyzing replicate aliquots of a sample, with R1 indicating the first analysis of the sample and R2 its corresponding duplicate.

4.20 Relative Response Factor (RRF)

RRF is the calibration factor calculating the response versus peak area as compared to a known internal standard.

$$RRF = \frac{(A_s C_{is})}{(A_{is} C_s)},$$

where:

A_s = Response for the analyte to be measured,

A_{is} = Response for the internal standard,

C_{is} = Concentration of the internal standard, µg/L, and

C_s = Concentration of the analyte to be measured, µg/L.

4.21 Sample Blanks

Sample blanks should be used when characteristics such as color or turbidity interfere with a determination. In a spectrophotometric method, for example, the natural absorbency of the sample is measured and subtracted from the absorbency of the developed sample.

4.22 Surrogates

Surrogates are measured amounts of certain compounds added before sample preparation or extraction. Analysts measure the recovery of the surrogate to determine systematic extraction problems.

5.0 RESPONSIBILITIES

5.1 The Division Leader

The Division Leader's responsibility is to ensure that all activities performed by ERD at the Livermore Site and Site 300 are performed safely and comply with all pertinent regulations and procedures, and provide the necessary equipment and resources to accomplish the tasks described in this procedure.

5.2 Quality Control (QC) Chemists

The ERD QC Chemists are responsible for reviewing 100% of the analytical data for technical adequacy, internal consistency and quality, determining and flagging data quality and requesting additional information from the analytical laboratories if there are suspect data points or problematic QC results.

6.0 PROCEDURE

6.1 Quality Criteria

To evaluate the validity of the reported analytical results, the status of the following criteria, which determine the quality of the analytical data, needs to be ascertained:

A. Integrity and stability of the samples(s) analyzed.

B. Performance of the instrument(s) used for analyses.

C. Internal quality control checks.

D. Identification and quantification of the analyte(s) in the sample(s) analyzed.

E. Precision and accuracy of the results reported.

F. Corrective action.

G. Deliverables.

H. Performance evaluation of the laboratory.

6.2. Integrity and Stability of Sample(s) Analyzed

To establish the integrity and stability of the environmental samples analyzed, the CAL will provide the following:

A. Signed Chain-of-Custody (CoC) form for each sample received.

B. Date and time of both extraction and analysis of each sample to ensure the appropriate holding times (if applicable) are met.

C. Condition of sample upon receipt form.

6.3. Performance of the Instruments(s) Used for Analysis

Analytical methodology for analyzing the samples will determine the type of instrument(s) to be used by the laboratory. To demonstrate the working condition of instrument(s) during analysis, the laboratory will document the following:

A. For all analyses, the detection limits for the selected suite of analysis and other constituents of interest analyzed and the method used to determine detection limits.

B. Identification of each instrument used for analysis.

C. Data for the initial and continuous calibration of the instrument.

6.3.1 The continuous and initial calibration requirements will depend on the analytical methodology used. The following are calibration criteria found in References 3.2 and 3.3:

The standard sources used in initial calibration shall be NIST-traceable Standard Reference Materials, or equivalent; however, source(s) used in calibration verification are not required to be NIST-traceable, unless measurements of these sources are directly used in calculation of analytical sample data results.

A. Volatile Organics by GC/MS

Instrument sensitivity should be checked with a specific compound such as bromofluorobenzene (BFB) every 12 h of operation. Retention time, peak area and shape, and isotope ratios should be examined. A mass calibration should also be performed with a compound such as perfluorotributylamine. The initial calibration of the gas chromatograph/mass spectrometry (GC/MS) is conducted as necessary, using five concentrations. Response factors for the following target compounds should be examined: four system performance check compounds (SPCCs) and five calibration check compounds (CCCs). The volatile SPCCs are: chloromethane, 1,1-dichloroethane, 1,1,2,2-tetrachloroethane, and chlorobenzene. The volatile CCCs are: Vinyl chloride, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, and toluene. SPCC response factors should exceed 0.050. The percent relative standard deviation of the CCC response factors should be less than 30%. A calibration check is run every 12 h. The SPCC response factors should meet the same criteria as those in the initial calibration, and the CCC response factors may not deviate more than 25% from the average response factor of the initial calibration. The internal standard calibration method may be used to quantitative samples.

B. Base/Neutral and Acid Extractable Organics by GC/MS

Instrument sensitivity should be checked with a compound such as decafluorotriph-enylphosphine (DFTPP) every 12 h of operation. Retention time, peak area and shape, and isotope ratios should be examined. A mass calibration should then be performed with a compound such as perfluorotributylamine. The initial calibration of the GC/MS is conducted as necessary, using five concentrations. Target compound response factors for four SPCCs and 13 CCCs are examined. The semivolatile SPCCs are: N-nitroso-di-n-propyl amine, hexachlorocyclopentadiene, 2,4-dinitrophenol, and 4-nitrophenol. The semivolatile CCCs are: phenol, 1,4-dichlorobenzene, 2-nitrophenol, 2,4-dichlorophenol, hexa-chlorobutadiene, 4-chloro-m-cresol, 2,4,6-trichlorophenol, acenaph-thene, N-nitro-sodiphenylamine, pintrachlorophenol, fluoranthene, di-n-octylphthalate, and benzo(a)pyrene. The SPCC response factors should exceed 0.050. The relative standard deviation of the CCC response factors should be less than 30%. A continuing calibration check is run every 12 h. The SPCC response factors should meet the same criteria as those in the initial calibration.

C. Volatile Organics/Organochlorine Pesticides by Gas Chromatography

Initial calibration is performed with a minimum of three and a maximum of five concentrations. The calibration curve must have a correlation factor of 0.990 or greater or have a %RPD for the RRF <20%. Each day, a continuing calibration standard is run prior to running the samples. The difference between the average response factor of the initial standard curve and the response factor of the continuing calibration must fall within the limits established by the analytical laboratory. The internal standard calibration method may be used to quantitative samples.

D. Metals by Inductively Coupled Plasma (ICP)

Prior to sample analysis, a calibration curve should be run. A standard should be run with every ten samples. The apparent concentration of this standard must be within 10% of the true concentration. Comparability studies should be carried out frequently to validate the concentration of commercial standards.

E. Metals by Graphite Furnace and Flame

Prior to sample analysis, a calibration curve of at least three standards is run. The calibration curve must have a correlation coefficient of 0.995 or greater. A single standard is then run every ten samples. The apparent concentration of this standard must lie within 10% of the true concentration. Standards are prepared by diluting commercially available solutions. Comparability studies are carried out frequently to validate the concentrations of the commercial standards.

F. Colorimetric Analyses

Cyanide, phenolics, nitrate, nitrite, and phosphates fall into this category. A calibration curve of at least three standards is prepared daily. The correlation coefficient of the curve must be 0.995 or greater.

G. Gravimetric Analyses

Oil and grease, dissolved solids, and suspended solids fall under gravimetric analysis. These analyses depend primarily on the accuracy of the balance used. For this reason, balances should be calibrated annually and checked before each use with class "S" weights. The recorded weight must agree within 0.1% of the expected weight.

H. pH

The pH meter should be calibrated with two buffers separated by three pH units prior to the day's analysis. The reading must be within 0.1 unit of the true value.

6.4 Internal Quality Control Checks

To ensure the quality of the analysis, internal quality control checks should be implemented as part of the analysis, and the laboratory will document the following:

A. At least one method blank analyzed in every analytical batch of samples or whenever system contamination is suspected following a high level sample.

B. Sample blanks when indicated by the analytical method.

C. Calibration blanks.

D. Internal standards. Internal standard calibration should be used for volatile organics, chlorinated pesticides, and GC/MS extractables.

E. Surrogate recovery. Surrogates should be added to all samples analyzed for chlorinated pesticides, GC/MS extractables and volatiles, and GC volatiles.

F. Matrix spike accuracy as percent recovery (%RCV) and precision as percent relative standard deviation (%RSD) when indicated by the analytical method.

G. Duplicates when matrix spikes are inappropriate.

H. LCSs should be prepared and analyzed with every batch of samples.

6.5 Identification and Quantification of the Analyte(s) in the Sample(s) Analyzed

6.5.1 If the sample(s) was analyzed by GC/MS, the laboratory will document the following:

A. Information about extraction method and dilution/concentration factor in the extraction of the sample prior to the analysis.

B. Unenhanced and enhanced mass spectrum of each compound of interest identified in the sample.

C. Quantification report (i.e., data system printouts) for the sample analyzed.

D. Laboratory-generated standard spectra for all compounds of interest identified in the environmental samples.

E. Identification of the date, time, and instrument used for the analysis and the analyst.

6.5.2 If the sample(s) were analyzed by a GC method, the laboratory will document the following:

A. Information about extraction method and dilution/concentration factor in the extraction of the sample prior to analysis.

B. Sample chromatogram with all compounds of interest peaks identified.

C. Raw data (i.e., integration reports) showing retention time and peak area/peak height counts for each identified compound of interest peak.

D. Identification of the date, time, and instrument used for the analysis and the analyst.

6.5.3 If the samples are analyzed by ICP, Flame Atomic Absorption Spectroscopy, or Graphite Furnace, the laboratory will document the following:

A. Information about digestion method and dilution/concentration factor in the digestion of the sample prior to the analysis.

B. Sample chromatogram with sample peak displayed.

C. Identification of the date, time, and instrument used for the analysis and the analyst.

6.6 Precision in Analysis and Accuracy of the Results Reported

6.6.1 To assess the significance of the analytical data, the precision, accuracy, and completeness must be taken into account. This assessment of the data is performed by the ERD's QC Chemists.

6.6.2 Precision analysis addresses the question, "Given the same sample or sample type, how well can the laboratory replicate its work?" Precision is generally discussed in terms of standard deviation or RSD%.

6.6.3 The estimation of precision is accomplished by analyzing duplicates of the same sample or collocated samples. Using collocated pairs is more practical for estimating the standard deviation of an analytical method because 1) samples are readily available in the laboratory, and 2) they allow the estimation of precision for an analysis based on a sample type rather than on a specific sample. If duplicates are analyzed for the same sample, this gives only information about the method's precision for that sample. Thus, the use of collocated pairs gives a more correct view of the overall analysis.

6.6.4 The calculation to estimate the standard deviation of each method in the laboratory is as follows:

$$s = \text{Square root} \left[\frac{\sum d^2}{2k} \right],$$

where:

k = Number of sets of duplicate measurements.

d = Difference of duplicate measurements.

s = Standard deviation.

6.6.5 Once the standard deviation of a method is determined, control limits can be established on individual duplicate pairs. The warning limit should be set at two standard deviations and the control limit at three standard deviations. (Only absolute standard deviation is of concern, rather than positive or negative values). These are the limits that are used to determine whether the system was in control and how the data are to be qualified.

6.6.6. Accuracy. Spike recovery determinations, regular analysis of laboratory control standards, and use of external check samples contribute to the general assurance that the accuracy of a determination is within acceptable limits. A determination's accuracy also depends on factors external to the laboratory, such as sampling and storage conditions.

6.6.7 Use of accumulated data from the spike analyses allows control limits to be established for the accuracy of an analysis. These control limits may then be plotted as control charts. After calculating the average recovery and the standard deviation of the recovery, warning limits should be set at two standard deviations. Each spike or standard recovery should be compared to the control limits to determine if the analysis is currently within acceptable limits. Control charts of LCS recoveries are useful in determining bias or trends over a period of time. These are the limits that are used to determine whether the system was in control and how the data are to be qualified.

6.7. Data Review and Corrective Action Performed by the CAL

6.7.1 The CAL should maintain control limits for laboratory control standards, method blanks, spike recoveries, duplicates, and surrogate recoveries. In addition, many analytical methods have QC criteria for calibrations, sensitivity checks, and other method-specific quality checks that are performed routinely. Corrective action is a process that is applied when a QC outlier or systematic error is detected.

6.7.2 The following are examples of more serious quality issues, and are dealt with within a formal Corrective Action Program by the management of the laboratory: systematic failures of a method, issues of method compliance, consistent contamination that the analyst cannot resolve, QC issues raised in audit reports, or QC failure that impacts data already reported.

6.7.3 Method Blank Data Review and Corrective Action (Organic Analysis):

A. Action in the case of unsuitable blank results depends on the circumstances and origin of the blank. No positive sample results should be reported unless the concentration of the compound in the sample exceeds ten times the amount in any blank for the common contaminants listed below, or five times the amount for other compounds. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results must not be corrected by subtracting any blank value. Specific actions are as follows:

1. If a compound is found in a blank but not found in the sample, no action is taken.

2. Any compound (other than the five listed below) detected in the sample, which was also detected in any associated blank, must be qualified when the sample concentration is less than five times the blank concentration. For the five common laboratory contaminants (methylene chloride, acetone, toluene, 2-butanone, and common phthalate esters), the results are qualified by elevating the limit of detection when the sample concentration is less than ten times the blank concentration.

B. The CAL data reviewer should note that the blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. These factors must be taken into consideration when applying the 5× and 10× criteria, such that a comparison of the total amount of contamination is actually made. If contamination is greater then the above specification, the samples should not be run until the system falls within the specifications.

C. If gross contamination exists (i.e., saturated peaks by GC/MS), all compounds affected should be flagged as unusable, due to interference, in all samples affected. In this case, the system should be decontaminated and recalibrated, and the samples, including new blanks, should be re-extracted if needed and reanalyzed.

D. If inordinate amounts of other compounds are found at low levels in the blank(s), it may be indicative of a problem at the laboratory and should be noted in the data review comments, which are forwarded to LLNL project personnel.

E. Similar consideration should be given to tentatively identified compounds—a compound not on the target compound list, which are found in both the sample and associated blank(s).

F. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of contaminant. The result must not be corrected by subtracting any blank value.

6.7.4 Method Blank Data Review and Corrective Action (Metal Analysis):

Action in the case of unsuitable blank results depends on the circumstances and origin of the blank. Sample results greater than the instrument detection limit (IDL) but less than five times the amount in any blank should be qualified as not detected above the level of the associated value. The associated value is either the sample quantitation limit or the sample detection limit. If contamination is greater than the above specification, the samples should not be run until the system falls within the specifications.

6.7.5 Laboratory Control Standards Data Review and Corrective Action (Organic and Metal Analysis):

If an LCS does not fall within the acceptance guidelines, then the LCS should be rerun. If the LCS still fails to fall within the given specification, the system should be recalibrated and the samples reanalyzed.

6.7.6 Surrogate Recovery Data Review and Corrective Action (Organic Analysis):

For surrogate spike recoveries out of specification, the following approaches are suggested based on a review of all data from the case, especially considering the apparent complexity of the sample matrix:

A. If at least two surrogates in a base/neutral or acid fraction or in a surrogate in the volatile fraction are out of specification, but have recoveries greater than 10%:

   1. Positive results for that fraction are flagged as estimated quantities.

   2. Negative results for that fraction are flagged with the sample quantitation limit as estimated quantity, which may be inaccurate or imprecise. In this case, the sample would need to be reanalyzed.

B. If any surrogate in a fraction shows less than 10% recovery:

   1. Positive results for that fraction are flagged as estimated quantities.

   2. Negative results for that fraction are flagged as unusable. In this case, the sample would need to be reanalyzed.

6.7.7 Matrix Spike/Matrix Spike Duplicate Data Review and Corrective Action (Organic Analysis):

A. No action is taken on Matrix Spike/Matrix Spike Duplicate (MS/MSD) data alone to qualify an entire case. However, using informed professional judgment, the data reviewer may use the matrix spike and matrix spike duplicate results in conjunction with other QC criteria to determine the need for some qualification of the data.

B. The data reviewer should first try to determine to what extent the results of the MS/MSD affect the associated data. This determination should be made with regard to the MS/MSD sample itself, as well as specific analytes for all samples associated with the MS/MSD.

C. In those instances where it can be determined that the results of the MS/MSD affect only the sample spiked, qualification should be limited to this sample alone. However, it may be determined through the MS/MSD results that a laboratory is having a systematic problem in the analysis of one or more analytes, which affects all associated samples.

6.7.8 Matrix Spike Data Review and Corrective Action (Metal Analysis):

A. If the spike recovery is >125% and the reported sample results are less than IDL, the data are acceptable for use.

B. If the spike recovery is >125% or <75% and the sample results are greater than IDL, qualify the data for these samples as estimated quantity.

C. If the spike recovery falls within the range of 30 to 74% and the sample results are less than IDL, qualify the data for these samples as estimated quantity, which may be inaccurate or imprecise.

D. If spike recovery results fall <30% and the sample results are less than IDL, qualify the data for these samples as unusable. In this case, the sample and a matrix spike should be redigested and reanalyzed.

6.8 Data Review and Corrective Action Performed by ERD QC Chemists

6.8.1 One hundred percent of all analytical results are reviewed by the ERD QC Chemists (Attachment A). The QC Chemist shall evaluate and qualify the data, if necessary, using the ERD Data Qualifier Flags, which were developed using the EPA Contract Laboratory Program (CLP) flags as a guide. Attachment B lists the qualifier flags and defines when they are appropriate for use.

6.8.2 During the QC Chemists data review, the data are qualified using the Data Qualifier Flag Forms (Attachment C). The QC Chemist fills out the form, and forwards a copy to the Data Management Group (DMG) [this may be done electronically]. In addition, a copy of the qualification form is attached to the analytical results.

6.8.3 There are two types of corrective action forms:

1. The Data Review Request (DRR) form (Attachment D) is used when a problem or a question with analytical results occur.

2. The Quality Improvement (QI) form (Attachment E) is used for correcting problems other than those associated with analytical services (i.e., cost savings or quality improvement suggestions; changes to data in the database; broken or inadequate material received from vendors; sampling errors; equipment repair; treatment facility permit violations).

   Note: a DRR may warrant a QI form if a trend is identified.

6.8.4 When problems requiring CAL attention are identified, a DRR form is logged into the DRR logbook to obtain the next unique number, and the top section of the form is filled out by the QC Chemist. The DRR is then Faxed to the appropriate laboratory where a resolution to the problem can be documented on the lower half and Faxed back to LLNL. When the DRR is completed to the QC Chemist's satisfaction, the logbook entry is closed out and the completed form is placed in the DRR binder. A DRR should be written whenever there is a problem with the analytical results. The QC chemist shall use best professional judgment. When reviewing QC results a DRR may not always be necessary.

6.8.5 A QI form should be completed in the following manner:

A. Locate QI form on Q-Mail. Fill out indicating problem/condition, underlying cause, corrective action taken, as well as preventative measures necessary.

B. Send completed form to the Quality Assurance Implementing Coordinator (QAIC).

C. The QAIC will log it in the QI form logbook to include a brief summary of the problem, date open, and name of responsible supervisor.

D. The QAIC will print the QI form, assign a compliance code and log number, and have the responsible supervisor sign the form.

   Compliance Codes:

   001 = Equipment or system failure.

   002 = Defective materials or items.

   003 = Calibration deficiency.

   004 = Insufficient training.

   005 = Procedure noncompliance.

   006 = Inadequate procedure.

   007 = Documentation deficiency.

   008 = Lack of document or record control.

   009 = Traceability and chain-of-custody.

   100 = Other items not covered above.

E. Once the QI form is completed to the QAIC's satisfaction, the QAIC will close out the form with a signature.

F. A copy shall be forwarded to the EPD QA Manager and all other affected individuals.

G. A copy shall be placed in the ERD QI form binder.

6.8.6 The data are evaluated and qualified based on the following:

A. Was the sample analyzed within holding time? If not, the data should be flagged in the database ("H"). A DRR form (Attachment D) and/or a Quality Improvement Form should be filled out when appropriate.

B. Are the sample results representative of historical data? Check reported results against the DMG's tables of historical results. If the data are not consistent with the historical results, a DRR form should be sent to the laboratory and the invoice held until a resolution is received.

C. If surrogates are used, are they within control limits? If not, a DRR may be filled out.

D. Is the LCS within the set control limits? Check percent recovery (%R) against the control limits the laboratory has provided. If the LCS recovery is greater than %R upper control limit (UCL) for an analyte, check to see if the analyte is detected in the sample from the same batch number. If it is positive, qualify the data as being positively identified, but value is approximate ("J"). If the analyte is not detected, the data need not be qualified. If the LCS recovery is less than %R lower control limit (LCL) for an analyte, check to see if the analyte is detected in the sample from the same batch number. If it is positive, write a DRR and qualify the data as being positively identified, but value is approximate ("J") *and the associated non-detected compound(s) should be qualified as "R," meaning sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be verified.* If more than half the compounds in the LCS are not within the required recovery criteria, all associated data should be qualified "R."

E. Are the matrix spike and matrix spike duplicate accuracy within the set control limits? Check %R against the control limits the laboratory has provided. If the recovery is out of control for an analyte, qualify the data in the database ("L").

F. Are the matrix spike and matrix spike duplicate precision within the set control limits? Check relative percent difference (%RPD) against the control limits the laboratory has provided. If the %RPD is out of control for an analyte, qualify the data in the database ("O"). If the analyte is not detected in the samples, the data need not be qualified.

G. Is the method blank clean? If an analyte(s) is positive in the method blank, check to see if the analyte(s) is detected in the samples from the same batch number. If it is positive, qualify the data in the database ("B").

H. Are the trip, field, and/or equipment blank(s) clean? If an analyte(s) is positive in these blanks, check to see if the analyte(s) is detected in the associated samples. If it is positive, qualify the data in the database ("F").

6.8.7 When a DRR is issued to the laboratory and the results are revised, the revised report will undergo the same data review steps that are applied to the original sample data.

6.8.8 The results and QC data are separated by the QC Chemist for filing whenever possible. The upper right-hand corners of the results are marked with a "V" for

validated, initiated by reviewer and dated. The QC data are initialed by the reviewer, and both are sent to the DMG for distribution and storage.

6.8.9 Statistical Data Outliers are flagged as outliers by a computer program developed inhouse. This program shall be run quarterly at the QC Chemist's request. When outliers are flagged, the QC Chemist investigates the possibility of data entry or analytical laboratory errors via a DRR.

6.8.10 All data are flagged in the database with the appropriate analytical level (I–V). The appropriate analytical levels are associated with specific analytical techniques. Certain analytical levels are necessary to acquire data for particular uses (Attachment F). The analytical levels are defined as follows:

I Field screening or analysis using portable instruments. Results are often not compound specific and not quantitative, but results are available in real-time. It is the least costly of the analytical options.

II Field analysis using more sophisticated, portable analytical instruments: in some cases, the instruments may be set up in a mobile laboratory onsite. There is a wide range in the quality of data that can be generated, depending on the use of the suitable calibration standards, reference materials, and sample preparation equipment and the training of the operator. Results are available in real-time or several hours.

III All analyses performed in an analytical laboratory. Level III analyses may or may not use CLP procedures, but do not usually utilize the validation or documentation procedures required of CLP Level IV analysis. The laboratory may or may not be a CLP laboratory.

IV CLP routine analytical services (RAS). All analyses are performed in an off-site CLP analytical laboratory following CLP protocols. Level IV is characterized by rigorous QA/QC protocols and documentation.

V Analysis by non-standard methods. All analyses are performed in an off-site analytical laboratory, which may or may not be a CLP laboratory. Method development or method modification may be required for specific constituents or detection limits. CLP special analytical services are Level V.

6.8.11 In addition to checking the results from the analytical laboratory against quality criteria and historical results, the analytical report is also checked against all contractual requirements before the data are accepted for use.

6.9 Deliverables

6.9.1 Case Narrative, written on laboratory letterhead, may include:

A. LLNL's sample identification and corresponding laboratory identification.

B. Parameters analyzed for each sample and the methodology used.

C. Detailed description of all problems encountered.

D. Discussion of possible reasons for any QA/QC criteria outside acceptance limits.

E. Observations regarding any occurrence that may affect sample integrity or data quality.

F. Whether holding times were exceeded.

G. The release of the data authorized by the laboratory manager.

6.9.2 Chain-of-Custody (CoC) Documentation

A. Legible copies of the CoC.

B. The date of receipt.

C. The observed sample condition at the time of receipt described on the CoC.

6.9.3 Summary of Results

A. LLNL's sample ID and the corresponding laboratory ID.

B. Sample matrix.

C. Date of sample extraction, if applicable.

D. Date and time of analysis.

E. ID of the instrument used for analysis.

F. Dilution or concentration factor of the samples.

G. Method detection limits or quantitation limits.

H. Definitions for any data qualifiers used.

I. Analytical results.

J. Any deviations from specified methodology (i.e., deviations in GC detectors or specifications).

6.9.4 Summary of QA/QC Results

A. LLNL's sample ID and corresponding laboratory ID.

B. QC batch number if applicable.

C. Method blanks.

D. Surrogate recoveries.

E. Matrix spike, spike duplicate, or duplicates.

F. Laboratory control samples or standards.

G. Laboratory QC control limits.

H. Continuing calibration samples.

6.9.5 In addition, the laboratory shall maintain the following information, which shall be made available upon request:

A. Continuing calibration samples.

B. Initial instrument calibration.

C. Retention time windows determination.

D. Compound identification (retention times and concentration of each analyte detected).

F. Method detection limit determinations.

G. Control charts.

H. GCMS tuning data.

6.9.6 Quarterly, the ERD QC Chemists have the option to request Level IV QC summary tables and raw calibration data for a select number of data packages. Semiannually, the QC Chemist will perform an evaluation of all QA/QC data, including calibration information and raw data validation, at the analytical laboratory on a select number of data packages. This number will be based on analytical laboratory performance and the QC Chemist's professional judgment. The packages to be reviewed are to be representative of the work being performed.

6.10 Performance Evaluation of the Analytical Laboratories

6.10.1 Check Standards will be used to assess the performance of the laboratories used. Laboratories may be evaluated on a quarterly basis (or less frequently) by the following means: participation in a recognized EPA check program or DOE EML evaluation program, or single blind or double blind samples submitted by LLNL from an off-site vendor. Where unavailable, an LLNL check standard may be generated with its preparation/procedure logged into ERD document control. Frequency of evaluation will be based on criticality and cost.

6.10.2 Selection of the appropriate check sample will be determined on the basis of the criticality of the analysis and the performance of the laboratory the previous calendar quarter as determined by the QC Chemist(s) for LLNL. The analyte(s) and matrix will also be selected by the performance of the laboratory the previous quarter. The recovery limits as specified by the certified source (i.e., EPA, DOE, Environmental Resource Associates, etc.) shall be used as the acceptance criteria. Certification documents shall be filed in ERD document control.

6.10.3 Check Standards shall be NIST traceable or equivalent. All dilutions of the standards shall be performed by an off-site vendor, the laboratory performing the analysis, or by LLNL personnel with a QC Chemist-approved procedure, which is filed in ERD document control.

6.10.4 Results shall be used to evaluate the laboratories. Nonperformance results will be addressed through a QI form and communicated to the analytical laboratory. All results will be sent to the procurement officer for analytical contracts, EPD Department QA office, and the ERD Division QA Manager for further action. Failure of a laboratory to correct any findings after three quarters shall be grounds for procurement resolution.

6.11 QA Reports to Management

6.11.1 The QC Chemist submits a report that assesses the quality of ERD Project data at least annually. This report summarizes the performance of QA measures and data quality for sampling and analysis activities for a specified time period, as reported by both the on- and off-site analytical laboratories. Performance of QA measures are reported in terms of precision as percent relative standard deviation (%RSD), accuracy as percent recovery (%RCV), and completeness.

6.11.2 The report summarizes performance on:

A. Equipment Blanks
B. Trip Planks
C. Field Blanks
D. Interlaboratory Collocated Samples
E. Intralaboratory Collocated Samples
F. Matrix Spikes
G. Method Blanks
H. Performance Evaluation Samples

7.0 QA RECORDS

The following are QA records and shall be maintained in accordance with Reference 3.1:

7.1 CoC forms
7.2 Logbooks
7.3 Original analytical results
7.4 Completed DRR and QI forms
7.5 Data Qualifier Flag forms
7.6 Check sample results
7.7 QA reports to management

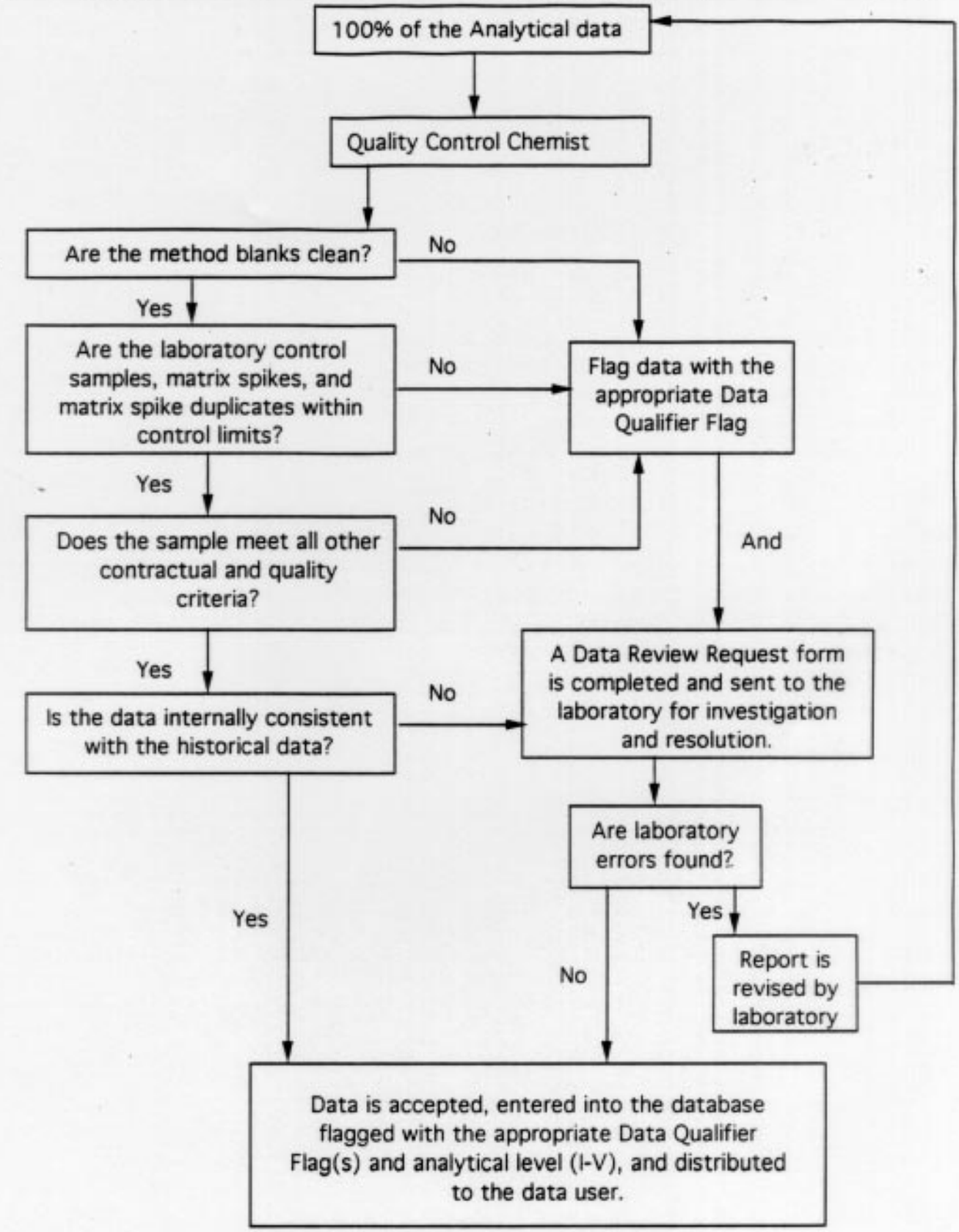
7.6 Laboratory Performance/Evaluation Data

8.0 ATTACHMENTS

Attachment A—Validation Flow Chart
Attachment B—Data Qualifier Flags
Attachment C—Data Qualifier Flag Form
Attachment D—Data Review Request Form
Attachment E—Quality Improvement Form
Attachment F—Summary of Analytical Levels Appropriate to Data Uses

Attachment A

Validation Flow Chart



Flow chart of data through the data validation/verification process.

Attachment B

Data Qualifier Flags

Flag	Definition	Indicates uncertain: Identity?	Conc.?
B	Analyte found in method blank[a]	no	yes
C	The analytical results for this sample are not in agreement with the intra or interlaboratory collocated sample results and the historical data for this location.	may vary	yes
D[b]	Analysis performed at a secondary dilution or concentration (i.e., vapor samples).	no	no
E	Concentration exceeds calibration range.	no	yes
F	Analyte found in field blank, trip blank, or equipment blank[a]	no	yes
G	Quantitated using fuel calibration, but does not match typical fuel fingerprint (fuel maybe gasoline, diesel, motor oil, etc.).	yes	yes
H[b]	Sample analyzed outside of holding time, sample results should be evaluated.	no	yes
I	Surrogate recoveries were outside of QC limits.[c]	no	yes
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.[d]	no	yes
L	Spike accuracy not within control limits.[e]	No action is taken by data user on the MS/MSD data alone.	
O	Duplicate spike or sample precision not within control limits.[e]		
P	Indicates that the absence of a data qualifier flag does not mean that the data does not need qualification, but that the implementation of electronic data qualifier flags was not yet established.		
R	Sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be verified.[d]		
S	The analytical results from this sample are suspect. Supply reasoning on form.	yes	yes
T	Analyte is tentatively identified compound; result is approximate.	yes	yes
U[b]	Compound was analyzed for, but not detected above the detection limit.	yes	yes

[a] If analytes are found in the method, field, equipment, or trip blank, flag positive sample results only.

[b] Automatically flagged in the database.

[c] When surrogate recoveries are below the lower control limit (LCL), associated sample results should be flagged "IR" and positive sample results should be flagged "IJ". When surrogate recoveries are above the upper control limit (UCL), the positive sample results should be flagged "IJ". When QC sample surrogates are out of control, all supporting information (i.e. MS/MSD accuracy and precision, LCS accuracy, and sample location historical data) should be considered to determine if the associated samples were affected.

[d] If the LCS recovery is greater than %R UCL, then positive sample results for the affected compound(s) should be qualified with a "J" for being positively identified, but value is approximate. If the LCS recovery is less than %R LCL, then positive sample results for the affected compound(s) should be qualified with a "J" for being positively identified, but value is approximate and the associated non-detected compound(s) should be qualified "R". If more than half of the compounds in the LCS are not within the required recovery criteria, then all associated data should be qualified "R".

[e] Both positive and non-detect sample results should be flagged when the MS/MSD recoveries or precision are out of control.

Attachment C

Data Qualifier Flag Form

Todays Date:_____

DATA QUALIFIER FLAG FORM

Circle the appropriate qualifier flags and fill out information below.

Flag	Definition
B	Analyte found in method blank
F	Analyte found in field blank, trip blank, or equipment blank
G	Quantitated using fuel calibration, but does not match typical fuel fingerprint.
I	Surrogate recoveries were outside of QC limits.
J	The analyte was positively identified; the associated numerical value is the approximate concentration of the analyte in the sample.
L	Spike accuracy not within control limits.
O	Duplicate spike or sample precision not within control limits.
R	Sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be verified.
S	The analytical results from this sample are suspect.
T	Analyte is tentatively identified compound; result is approximate.

Laboratory Code: (circle one) BB, CL, CS, FG, LH, MA or other:_____

QC Chemist Initials:_____Requested Analysis:_____

Analyte(s)/Code:_____

Explanation (i.e., matrix interference, methlylene chloride in blank, etc.):_____

Log Number of Affected Samples:_____

For Data Management Use Only:

Entered: Initials_____Date:_____

Elect. Confirmed: Initials:_____Date:_____

Attachment D

Data Review Request Form

LLNL Site 300 Analytical Laboratory Data Review Request

Request Number: S3DRR95-0006
Today's Date: May 28, 1996
Logbook Number: DA-059

Analytical Laboratory: CLS

Sample ID(s):	Log Number(s):	Date(s) Sampled:	CoC Number(s):
NC7-71	CSM8290-4A	3/29/95	AD141
NC7-44	CSM8290-5A	3/29/95	AD141
NC7-52A	CSM8290-7A	3/29/95	AD141

Description of Request/Problem:

Our usual procedure for you to verify any positive detections in "clean wells" did not work recently because the sampler did not indicate on the CoC that NC7-71 and NC7-44 are clean wells. NC7-52A is also historically clean. The most recent analyses of these samples shows TCE detections of 0.51 ppb in NC7-44 and 52A and 0.8 ppb ethylbenzene and 0.63 ppb xylene in NC7-71. Please check the data and run log to determine if a high level sample(s) were run on the instrument/port and the possibility of carryover or system contamination.

Please fill out the bottom half of this form with your resolution and FAX it back to me, Valerie Kiszka at (510) 423-5764 so I can close out this Data Review Request. Thank you!

Date Resolution Required:	Requester:

Resolution:

Date:	Laboratory Representative:

Attachment E

Quality Improvement Form

Quality Improvement Form

Section 1 - Instructions on how to use this form:

In the space below, explain problem, condition, cost savings or quality improvement suggestion and identify:

1) Underlying cause (if known)
2) Corrective action needed or taken
3) Preventative measures (when applicable)

Send to the responsible Group Leader for approval

Section 2 - To be filled out by the responsible Group Leader:

Responsible Group Leader:

Form Approved? If yes, initial here: and forward to Valerie Kiszka.

If no, send back to preparer for revision, and then back to the Group Leader.

Section 3 - To be filled out by Valerie Kiszka:

QAIC Concurrence:

Log Number:

Compliance Code:

Attachment F

Summary Table of Analytical Levels

Attachment F-1. Summary of analytical levels appropriate to data uses.

Data uses	Analytical level	Type of analysis	Limitations	Data quality
Site characterization Monitoring during implementation	Level I	• Total organic/ inorganic vapor detection using portable instruments • Field test kits	• Instruments respond to naturally occurring compounds	• If instruments calibrated and data interpreted correctly, can provide indication of contamination
Site characterization Evaluation of alternatives Engineering design Monitoring during implementation	Level II	• Variety of organics by GC, inorganics by AA, XRF • Tentative ID, analyte-specific • Detection limits vary from low ppm to low ppb	• Tentative ID • Techniques/ instruments limited mostly to volatiles, metals	• Dependent on QA/GC steps employed • Data typically reported in concentration ranges
Risk assessment Site characterization Evaluation of alternatives Engineering design Monitoring during implementation	Level III	• Organics/ inorganics using procedures other than CLP can be analyte- specific • RCRA characteristics	• Tentative ID in some cases • Can provide data of same quality as Level IV	• Similar detection limits to CLP • Less rigorous QA/QC
Risk assessment Evaluation of alternatives Engineering design	Level IV	• HSL organics/ inorganics by GC/MS, AA, ICP • Low ppb detection limit	• Tentative ID of non-HSL parameters • Some time may be required for validation of packages	• Goal is data of known quality • Rigorous QC
Risk assessment	Level V	• Nonconventional parameters • Method-specific detection limits • Modification of existing methods	• May require method development/ modification • Mechanism to obtain services requires special lead time	• Method-specific